Enantioselective Organocatalytic Cyclopropanations. The Identification of a New Class of Iminium Catalyst Based Upon Directed Electrostatic Activation

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Supporting Information

General Information. All solvents were purified according to the method of Grubbs.[1] Organic solutions were concentrated under reduced pressure on a Büchi rotary evaporator. Chloroform was purchased from Aldrich and used without purification. Chromatographic purification of products was accomplished using forced-flow chromatography on ICN 60 32-64 mesh silica gel according to the method of Still.[2] Thin-layer chromatography (TLC) was performed on EM Reagents 0.25 mm silica gel 60-F plates. Visualization of the developed chromatogram was performed by fluorescence quenching, anisaldehyde, ceric ammonium molybdate, or $KMnO_4$ stain.

^1H and ^{13}C NMR spectra were recorded on Varian Mercury 300 (300 MHz and 75 MHz respectively) as noted, and are internally referenced to residual protio solvent signals. Data for ^1H are reported as follows: chemical shift (δ ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), integration, coupling constant (Hz) and assignment. Data for ^{13}C NMR are reported in terms of chemical shift. IR spectra were recorded on a Perkin Elmer Paragon 1000 spectrometer and are reported in terms of frequency of absorption (cm^{-1}). Mass spectra were obtained from the California Institute of Technology Mass Spectral facility. Gas liquid chromatography (GLC) was performed on Hewlett-Packard 6850 Series gas chromatography equipped with a split-mode capillary injection system and flame ionization detectors using Bodman Chiraldex Γ-TA, Γ-DM, and Γ-BP (30 m x 0.25 mm) columns. High performance liquid chromatography (HPLC) was performed on a Hewlett-Packard 1100 Series chromatographs using a Chiracel AD column (25 cm) and AD guard (5 cm) as noted.

General Procedure: A 50 mL round-bottom flask equipped with a magnetic stir bar was charged with aldehyde (0.5 mmol) and chloroform (21 mL), then cooled to –10 °C and allowed to stir for 20 min before adding (*S*)-(–)-indoline-2-carboxylic acid (4.2 mg, 0.026 mmol) and 2-(dimethyl-λ⁴-sulfanylidene)-1-phenyl-ethanone[3] (23 mg, 0.127 mmol). The homogeneous solution was stirred at a constant temperature for 24 - 48 hours until complete consumption of the starting material was observed. The cold reaction mixture was then eluted with Et_2O through a short silica gel plug and the filtrate was concentrated *in vacuo*. The resulting yellow residue was purified by silica gel chromatography (solvents noted) to provide the title compounds.

(1*R*, 2*S*, 3*R*)-2-Benzoyl-3-propyl-cyclopropanecarbaldehyde (Table 1, entry 1): Prepared according to the general procedure from hexenal (59 μL, 0.50 mmol) to provide the title compound as a light yellow oil (23 mg, 85% yield, 95% ee, 30:1 d.r.) after silica gel chromatography (17% Et_2O/ hexanes). IR (film) 2960, 2930, 2872, 1702, 1669, 1597, 1580, 1449, 1363, 1224, 1176, 1120, 1078, 1019, 992, 699 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 9.35 (d, 1H, *J* = 6.8 Hz, CHO), 7.97-7.96 (m, 2H, ArH), 7.57 (t, 1H, *J* = 7.3 Hz, ArH), 7.46 (t, 2H, *J* = 7.8 Hz, ArH), 3.0 (dd, 1H, *J* = 5.9, 8.3 Hz, C**H**COPh), 2.51- 2.48 (m, 1H, C**H**$(CH_2)_2CH_3$), 2.11 (dt, 1H, *J* = 5.8, 5.8, 8.3 Hz, C**H**CHO), 1.6-1.44 (m, 4H, (C**H**$_2$)$_2$$CH_3$), 0.94 (m, 3H, $(CH_2)_2C$**H**$_3$); ^{13}C NMR (75 MHz, $CDCl_3$) δ 199.1, 196.0, 136.9, 133.4, 128.6, 128.2, 40.1, 34.6, 33.9, 29.1, 21.9, 13.5; HRMS (EI) exact mass calculated for ($C_{14}H_{16}O_2$) requires *m/z* 216.1150, found *m/z* 216.1153. $[\alpha]_D$ = –16.63 (c = 1.0, $CHCl_3$). The enantio- and diastereomeric ratios were determined by GLC using a Bodman Chiraldex β-DM (30 m x 0.25 mm) column (135 °C isotherm for 90 min ramp to 155 °C isotherm for 18 min, 1 mL/min); *Major* diastereomer: major enantiomer t_r = 101.9 min and *minor* enantiomer t_r = 104.7 min; *minor* diastereomer: major enantiomer t_r = 79.4 min.

(1*R*, 2*R*, 3*S*)-2-Allyloxymethyl-3-benzoyl-cyclopropanecarbaldehyde (Table 1, entry 2): Prepared according to the general procedure from (*E*)-4-Allyloxy-but-2-enal[4] (64 mg, 0.50 mmol) to provide the title compound as a colorless oil (24 mg, 77% yield, 91% ee, 21:1 d.r.) after silica gel chromatography (25% Et_2O/ hexanes). IR (film) 3065, 2859, 1705, 1672, 1597, 1580, 1450, 1389, 1352, 1225, 1114, 1086, 990, 930, 746, 704

cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 9.38 (d, 1H, J = 6.6 Hz, CHO), 8.03-7.99 (m, 2H, ArH), 7.62-7.57 (m, 1H, ArH), 7.51-7.46 (m, 2H, ArH), 5.93-5.82 (m, 1H, CH_2CH=CH_2), 5.27 (app. dq, 1H, J = 1.7, 1.7, 17.3 Hz, CH_2CH=C$\mathbf{H}_{trans}$), 5.21 (app. dq, 1H, J = 1.4, 1.4, 11.6 Hz, CH_2CH=C$\mathbf{H}_{cis}$), 4.03-3.99 (m, 2H, C$\mathbf{H_2}$CH=CH_2), 3.72 (dd, 1H, J = 5.5, 10.5 Hz, CH_2OCH_a), 3.58 (dd, 1H, J = 5.3, 10.4 Hz, CH_2OCH_b), 3.26 (dd, 1H, J = 6.3, 8.8 Hz, C**H**COPh), 2.78 (m, 1H, C**H**CH_2OCH_2), 2.33 (ddd, 1H, J = 6.3, 6.3, 8.8 Hz, C**H**CHO); ^{13}C NMR (75 MHz, $CDCl_3$) δ 198.8, 195.6, 136.8, 134.1, 133.6, 128.7, 128.4, 117.4, 71.8, 68.5, 36.5, 31.8, 27.7; HRMS (EI) exact mass calculated for ($C_{15}H_{16}O_3$) requires m/z [M-H] 243.1021, found m/z 243.1006. $[\alpha]_D$ = –8.67 (c = 1.0, $CHCl_3$). The enantio- and diastereomeric ratio was determined by GLC using a Bodman Chiraldex β-DM (30 m x 0.25 mm) column (157 °C isotherm for 120 min, 1 mL/min); *Major* diastereomer: major enantiomer t_r = 103.0 min and *minor* enantiomer t_r = 108.6 min; *minor* diastereomer: major enantiomer t_r = 70. 4 min.

(1*R*, 2*S*, 3*R*)-2-Benzoyl-3-methyl-cyclopropanecarbaldehyde (Table 1, entry 3): Prepared according to the general procedure from crotonaldehyde (44 μL, 0.52 mmol) at +4 °C to provide the title compound as a light yellow oil (16 mg, 67% yield, 90% ee, >19:1 d.r.) after silica gel chromatography (20% Et_2O/hexanes). IR (film) 3062, 2965, 2932, 2869, 1702, 1670, 1597, 1580, 1449, 1426, 1384, 1354, 1269, 1227, 1170, 1116, 1076, 1050, 1019, 988, 953, 743, 696 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 9.34 (d, 1H, J = 6.6 Hz, CHO), 7.98- 7.96 (m, 2H, ArH), 7.61- 7.57 (m, 1H, ArH), 7.50- 7.46 (m, 2H, ArH), 2.99 (dd, 1H, J = 6.0, 8.5 Hz, C**H**COPh), 2.52 (ddq, 1H, J = 6.1, 6.1, 12.1 Hz, C**H**CH_3), 2.1 (ddd, 1H, J = 6.4, 6.4, 8.8 Hz, C**H**CHO), 1.35 (d, 3H, J = 6.0 Hz, C$\mathbf{H}_3$); ^{13}C NMR (75 MHz, $CDCl_3$) δ 199.4, 196.1, 136.9, 133.5, 128.7, 128.2, 41.1, 39.6, 35.8, 23.7, 16.9; HRMS (EI) exact mass calculated for ($C_{12}H_{12}O_2$) requires m/z 188.0837, found m/z 188.0835. $[\alpha]_D$ = –5.78 (c = 1.0, $CHCl_3$). The enantiomeric ratio was determined by GLC using a Bodman Chiraldex β-TA (30 m x 0.25 mm) column (160 °C isotherm for 60 min, 1 mL/min); *Major* diastereomer: major enantiomer t_r = 37.8 min and *minor* enantiomer t_r = 39.2 min. The diastereomeric ratio was determined by ^1H-NMR analysis of the crude reaction mixture.

(1*R*, 2*S*, 3*R*)-2-Benzoyl-3-hex-5-enyl-cyclopropanecarbaldehyde (Table 1, entry 4): Prepared according to the general procedure from (*E*)-Nona-2,8-dienal[5] (157 mg, 0.41 mmol) in $CHCl_3$ (23 mL) at –10 °C using (*S*)-(–)-indoline-2-carboxylic acid (4.5 mg, 0.027 mmol) and 2-(dimethyl-λ^4-sulfanylidene)-1-phenyl-ethanone (25 mg, 0.139 mmol) to provide the title compound as a colorless oil (26 mg, 74% yield, 96% ee, 24:1 d.r.) after silica gel chromatography (17% Et_2O/hexanes). IR (film) 3073, 2928, 2856, 1702, 1670, 1597, 1580, 1449, 1359, 1226, 1176, 1120, 993, 911, 700 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) 9.35 (d, 1H, *J* = 6.6 Hz, CHO), 7.99-7.97 (m, 2H, ArH), 7.64-7.58 (m, 1H, ArH), 7.51-7.47 (m, 2H, ArH), 5.77 (app. dt, 1H, *J* = 6.6, 6.6, 10.2, 16.8 Hz, C**H**=CH_2), 5.0-4.92 (m, 2H, CH=C**H$_2$**), 3.02 (dd, 1H, *J* = 6.0, 8.5 Hz, C**H**COPh), 2.52 (ddt, 1H, *J* = 6.4, 6.4, 12.4 Hz, C**H**$(CH_2)_4CH=CH_2$), 2.16- 2.02 (m, 3H), 1.64-1.39 (m, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) 199.3, 196.0, 138.4, 136.9, 133.5, 128.7, 128.3, 114.7, 40.2, 34.7, 33.4, 31.9, 29.3, 28.3, 28.1; HRMS (EI) exact mass calculated for ($C_{17}H_{20}O_2$) requires *m/z* 256.1463, found *m/z* 256.1482. $[\alpha]_D$ = -19.47 (c = 1.0, $CHCl_3$). The enantio- and diastereomeric ratio was determined by GLC using a Bodman Chiraldex -DM (30 m x 0.25 mm) column (160 °C isotherm for 145 min, 1 mL/min); *Major* diastereomer: major enantiomer t_r = 127.6 min and *minor* enantiomer t_r = 131.3 min; *minor* diastereomer: major enantiomer t_r = 89. 5 min.

(1*R*, 2*S*, 3*R*)-2-Benzoyl-3-phenyl-cyclopropanecarbaldehyde (Table 1, entry 5): Prepared according to the general procedure from cinnamaldehyde (87 L, 0.69 mmol) in $CHCl_3$ (42 mL) at –10 °C using (*S*)-(–)-indoline-2-carboxylic acid (8.2 mg, 0.05 mmol) and 2-(dimethyl-λ^4-sulfanylidene)-1-phenyl-ethanone (45 mg, 0.25 mmol) to provide the title compound as a yellow oil (46 mg, 73% yield, 89% ee, 33:1 d.r.) after silica gel chromatography (20% Et_2O/hexanes). IR (film) 3061, 3032, 2861, 1702, 1673, 1596, 1580, 1499, 1426, 1393, 1354, 1263, 1226, 1172, 1128, 1019, 996, 744, 696 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) 9.59 (d, 1H, *J* = 6.3 Hz, CHO), 8.01-7.98 (m, 2H, ArH), 7.61-7.21 (m, 8H, ArH), 3.60 (t, 1H, *J* = 6.0, 6.0 Hz, C**H**Ph), 3.49 (dd, 1H, *J* = 6.3, 9.1 Hz, C**H**COPh), 2.68 (ddd, 1H, *J* = 6.3, 6.3, 9.1 Hz, C**H**CHO); ^{13}C NMR (75 MHz, $CDCl_3$) 198.0, 195.1, 136.8, 136.6, 133.7, 128.8, 128.7, 128.4, 127.5, 126.5, 40.8, 36.8, 32.4; HRMS (EI) exact mass calculated for ($C_{17}H_{14}O_2$) requires *m/z* 250.0994, found *m/z*

250.0998. $[\alpha]_D$ = –165.7 (c = 1.0, $CHCl_3$). The diastereomeric ratio was determined by GLC using a Bodman Chiraldex Γ-CD butyrl (30 m x 0.25 mm) column (175 °C isotherm for 110 min, 1 mL/min); major diasteromer t_r = 81.5 min and minor diastereomer t_r = 60.3 min. The enantiomeric ratio was determined by HPLC analysis of the alcohol, obtained by $NaBH_4$ reduction of the aldehyde, using a Chiracel AD and AD guard column (8% ethanol/hexanes, 1mL/min); major enantiomer t_r = 74.11 min and minor enantiomer t_r = 27.6 min.

(1*R*, 2*S*, 3*R*)-2-Benzoyl-3-isobutyl-cyclopropanecarbaldehyde (Table 1, entry 6): Prepared according to the general procedure from (*E*)-5-Methyl-hex-2-enal[6] (22 mg, 0.20 mmol) in $CHCl_3$ (33 mL) at –10 °C using (*S*)-(–)-indoline-2-carboxylic acid (6.5 mg, 0.04 mmol) and 2-(dimethyl-λ⁴-sulfanylidene)-1-phenyl-ethanone (36 mg, 0.2 mmol) to provide the title compound as a light yellow oil (29 mg, 63% yield, 96% ee, 43:1 d.r.) after silica gel chromatography (14% Et_2O/hexanes). IR (film) 2957, 2870, 1703, 1670, 1597, 1580, 1450, 1386, 1366, 1224, 1174, 1019, 996, 705 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 9.35 (d, 1H, *J* = 6.6 Hz, CHO), 7.99-7.96 (m, 2H, ArH), 7.63-7.56 (m, 1H, ArH), 7.52-7.45 (m, 2H, ArH), 3.0 (dd, 1H, *J* = 6.0, 8.5 Hz, C**H**COPh), 2.53 (ddt, 1H, *J* = 6.0, 6.0, 12.9 Hz, C**H**$CH_2CH(CH_3)_2$), 2.10 (app dt, 1H, *J* = 6.3, 6.3, 8.5 Hz, C**H**CHO), 1.77 (tq, 1H, *J* = 6.6, 13.1 Hz, C**H**$(CH_3)_2$), 1.48-1.37 (m, 2H), 0.95 (d, 6H, *J* = 6.6 Hz $(CH_2)_2C\mathbf{H}_3$); ^{13}C NMR (75 MHz, $CDCl_3$) δ 199.3, 196.1, 136.9, 133.5, 128.7, 128.2, 41.1, 40.3, 34.7, 28.3, 27.8, 22.3; HRMS (EI) exact mass calculated for ($C_{15}H_{18}O_2$) requires *m/z* 230.1307, found *m/z* 230.1286. $[\alpha]_D$ = –31.41 (c = 1.0, $CHCl_3$). The enantio- and diastereomeric ratio was determined by GLC using a Bodman Chiraldex Γ-BP (25 m x 0.25 mm) column (155 °C isotherm for 65 min, 1 mL/min); *Major* diastereomer: major enantiomer t_r = 44.6 min and *minor* enantiomer t_r = 46.0 min; *minor* diastereomer: major enantiomer t_r = 30.2 min.

(1*R*, 2*S*, 3*R*)-2-(4-Bromo-benzoyl)-3-propyl-cyclopropanecarbaldehyde (Table 1, entry 7): Prepared according to the general procedure from hexenal (80 μL, 0.69 mmol) in $CHCl_3$ (28 mL) at –10 °C using (*S*)-(–)-indoline-2-carboxylic acid (5.5 mg, 0.034 mmol) and 1-(4-Bromo-phenyl)-2-(dimethyl-λ⁴-sulfanylidene)-ethanone[3] (45

mg, 0.17 mmol) to provide the title compound as a colorless oil (34 mg, 67% yield, 92% ee, 72:1 d.r.) after silica gel chromatography (25% Et_2O/hexanes). IR (film) 2960, 2929, 2872, 1702, 1670, 1585, 1484, 1437, 1400, 1362, 1235, 1221, 1174, 1121, 1070, 1025, 1008, 993, 844, 783 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 9.34 (d, 1H, J = 6.6 Hz, CHO), 7.85-7.82 (m, 2H, ArH), 7.64-7.61 (m, 2H, ArH), 2.95 (dd, 1H, J = 6.0, 8.6 Hz, C**H**COPh), 2.54-2.46 (m, 1H, C**H**$(CH_2)_2CH_3$), 2.12 (ddd, 1H, J = 6.4, 6.4, 8.6 Hz, C**H**CHO), 1.60-1.42 (m, 4H, (C**H**$_2)_2CH_3$), 0.99-0.92 (m, 3H, $(CH_2)_2$C**H**$_3$); ^{13}C NMR (75 MHz, $CDCl_3$) δ 198.9, 195.1, 135.6, 132.0, 129.7, 128.7, 40.1, 34.5, 33.9, 29.3, 21.9, 13.6; HRMS (EI) exact mass calculated for ($C_{14}H_{15}BrO_2$) requires m/z 294.0255, found m/z 294.0291. $[\alpha]_D$ = –21.27 (c = 1.0, $CHCl_3$). The enantio- and diastereomeric ratio was determined by GLC using a Bodman Chiraldex γ-DM (30 m x 0.25 mm) column (165 °C isotherm for 110 min, 1 mL/min); *Major* diastereomer: major enantiomer t_r = 101.4 min and *minor* enantiomer t_r = 104.5 min; *minor* diastereomer: major enantiomer t_r = 76.2 min.

(1*R*, 2*S*, 3*R*)-2-(4-Methoxy-benzoyl)-3-propyl-cyclopropanecarbaldehyde (Table 1, entry 8): Prepared according to the general procedure from hexenal (80 μL, 0.69 mmol) in $CHCl_3$ (30 mL) at –10 °C using (*S*)-(–)-indoline-2-carboxylic acid (5.5 mg, 0.034 mmol) and 2-(Dimethyl-λ^4-sulfanylidene)-1-(4-methoxy-phenyl)-ethanone[7] (38 mg, 0.18 mmol) to provide the title compound as a colorless oil (28 mg, 64% yield, 93% ee, 11:1 d.r.) after gradient silica gel chromatography (20 to 50% Et_2O/hexanes). IR (film) 2960, 2932, 2872, 2764, 1702, 1660, 1600, 1575, 1463, 1437, 1363, 1310, 1262, 1239, 1169, 1116, 1025, 992, 846, 795 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 9.33 (d, 1H, J = 6.6 Hz, CHO), 7.96 (d, 2H, J = 9.1 Hz, ArH), 6.95 (d, 2H, J = 8.8 Hz, ArH), 3.88 (s, 3H, OC**H**$_3$), 2.98 (dd, 1H, J = 6.1, 8.6 Hz, C**H**COPh), 2.54-2.46 (m, 1H, C**H**$(CH_2)_2CH_3$), 2.07 (app dt, 1H, J = 6.3, 6.3, 8.3 Hz, C**H**CHO), 1.60-1.46 (m, 4H, (C**H**$_2)_2CH_3$), 0.99-0.92 (m, 3H, $(CH_2)_2$C**H**$_3$); ^{13}C NMR (75 MHz, $CDCl_3$) δ 199.6, 194.3, 163.8, 130.6, 130.0, 113.9, 55.5, 39.9, 34.4, 34.1, 28.8, 22.0, 13.7; HRMS (EI) exact mass calculated for ($C_{15}H_{18}O_3$) requires m/z 246.1256, found m/z 246.1257. $[\alpha]_D$ = –26.42 (c = 1.0, $CHCl_3$). The enantiomeric ratio was determined by GLC using a Bodman Chiraldex γ-DM (30 m x 0.25 mm) column (165 °C isotherm for 110 min, 1 mL/min); *Major*

diastereomer: major enantiomer t_r = 106.5 min and *minor* enantiomer t_r = 108.2 min. The diastereomeric ratio was determined by ^{1}H-NMR analysis of the crude reaction mixture.

(1*R*, 2*S*, 3*R*)-2-(2,2-Dimethyl-propionyl)-3-propyl-cyclopropanecarbaldehyde (Table 1, entry 9): Prepared according to the general procedure from hexenal (93 μL, 0.80 mmol) in $CHCl_3$ (33 mL) at –10 °C using (*S*)-(–)-indoline-2-carboxylic acid (6.5 mg, 0.04 mmol) and 1-(Dimethyl-λ^4-sulfanylidene)-3,3-dimethyl-butan-2-none[8] (32 mg, 0.20 mmol) to provide the title compound as a colorless oil (32 mg, 82% yield, 95% ee, 6:1 d.r.) after silica gel chromatography (20 % Et_2O/hexanes). IR (film) 2964, 2932, 2873, 1703, 1478, 1465, 1367, 1194, 1171, 1125, 1084, 1049, 1032, 998, 940, 901 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.30 (d, 1H, *J* = 6.6 Hz, CHO), 2.52 (dd, 1H, *J* = 6.0, 8.6 Hz, C**H**COPh), 2.31-2.21 (m, 1H, C**H**$(CH_2)_2CH_3$), 1.90 (ddd, 1H, *J* = 6.3, 6.3, 8.6 Hz, C**H**CHO), 1.50-1.40 (m, 4H, $(CH_2)_2CH_3$), 1.2 (s, 9H), 0.99-0.88 (m, 3H, $(CH_2)_2CH_3$); ^{13}C NMR (75 MHz, $CDCl_3$) δ 211.7, 199.9, 44.4, 39.9, 34.0, 33.5, 29.3, 26.1, 21.9, 13.6; HRMS (EI) exact mass calculated for ($C_{12}H_{20}O_2$) requires *m/z* 196.1463, found *m/z* 196.1453. $[\alpha]_D$ = –29.79 (c = 1.0, $CHCl_3$). The enantio- and diastereomeric ratio was determined by GLC using a Bodman Chiraldex β-DM (30 m x 0.25 mm) column (110 °C isotherm for 60 min, 1 mL/min); *Major* diastereomer: major enantiomer t_r = 28.9 min and *minor* enantiomer t_r = 33.6 min; *minor* diastereomer A: major enantiomer t_r = 19.9 min and *minor* enantiomer t_r = 19.4 min; *minor* diastereomer B: major enantiomer t_r = 52.7 min and *minor* enantiomer t_r = 48.0 min.

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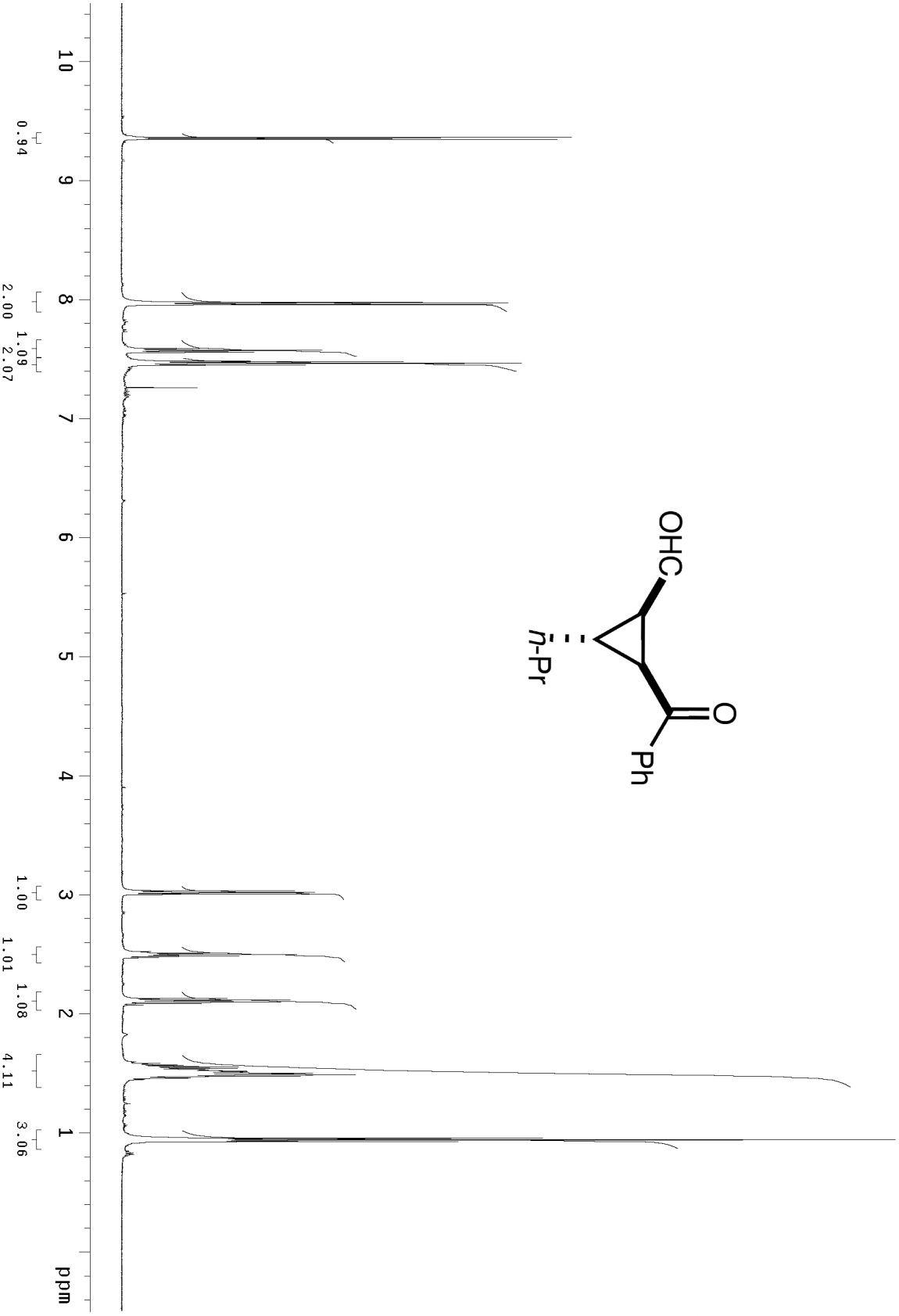
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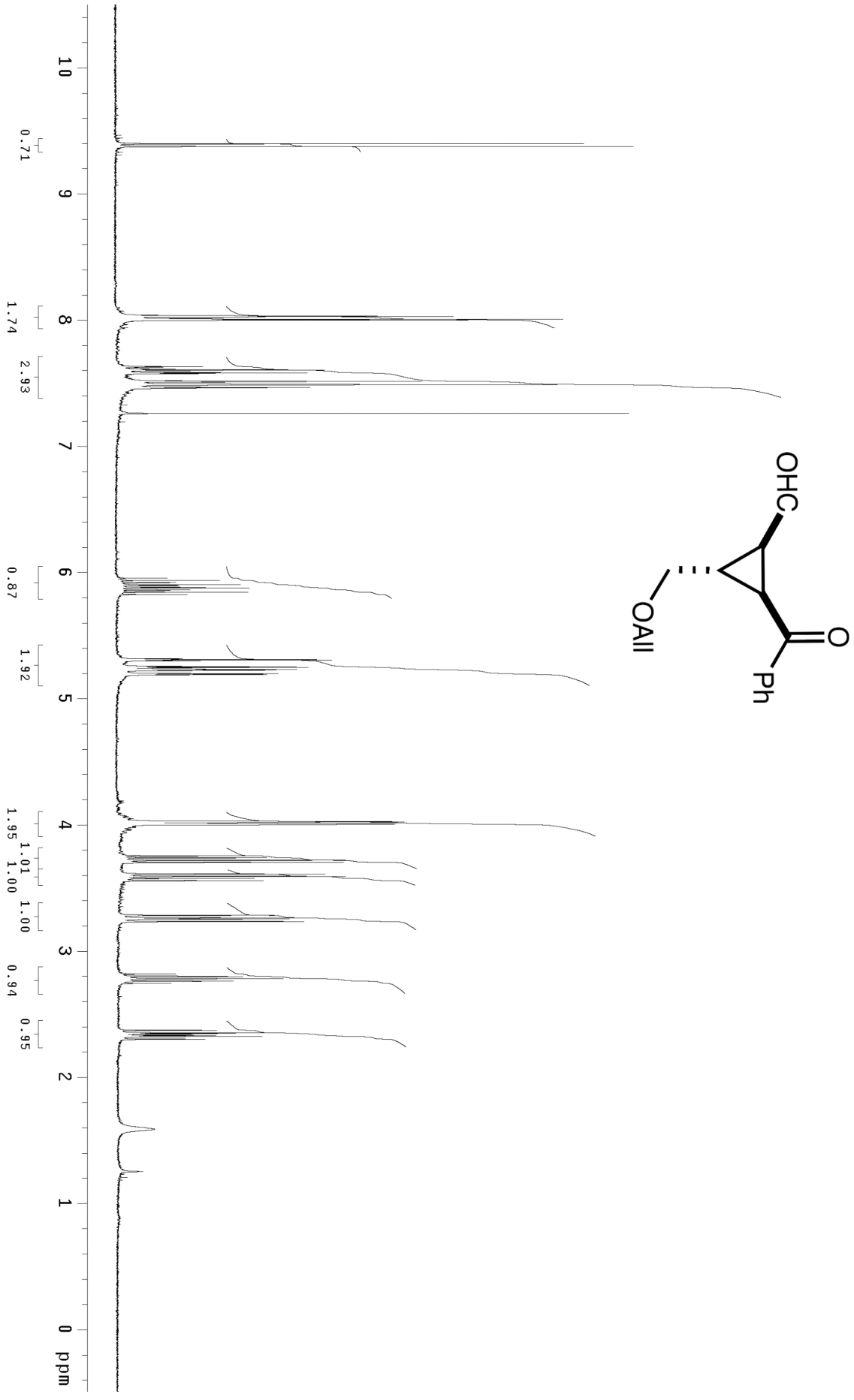
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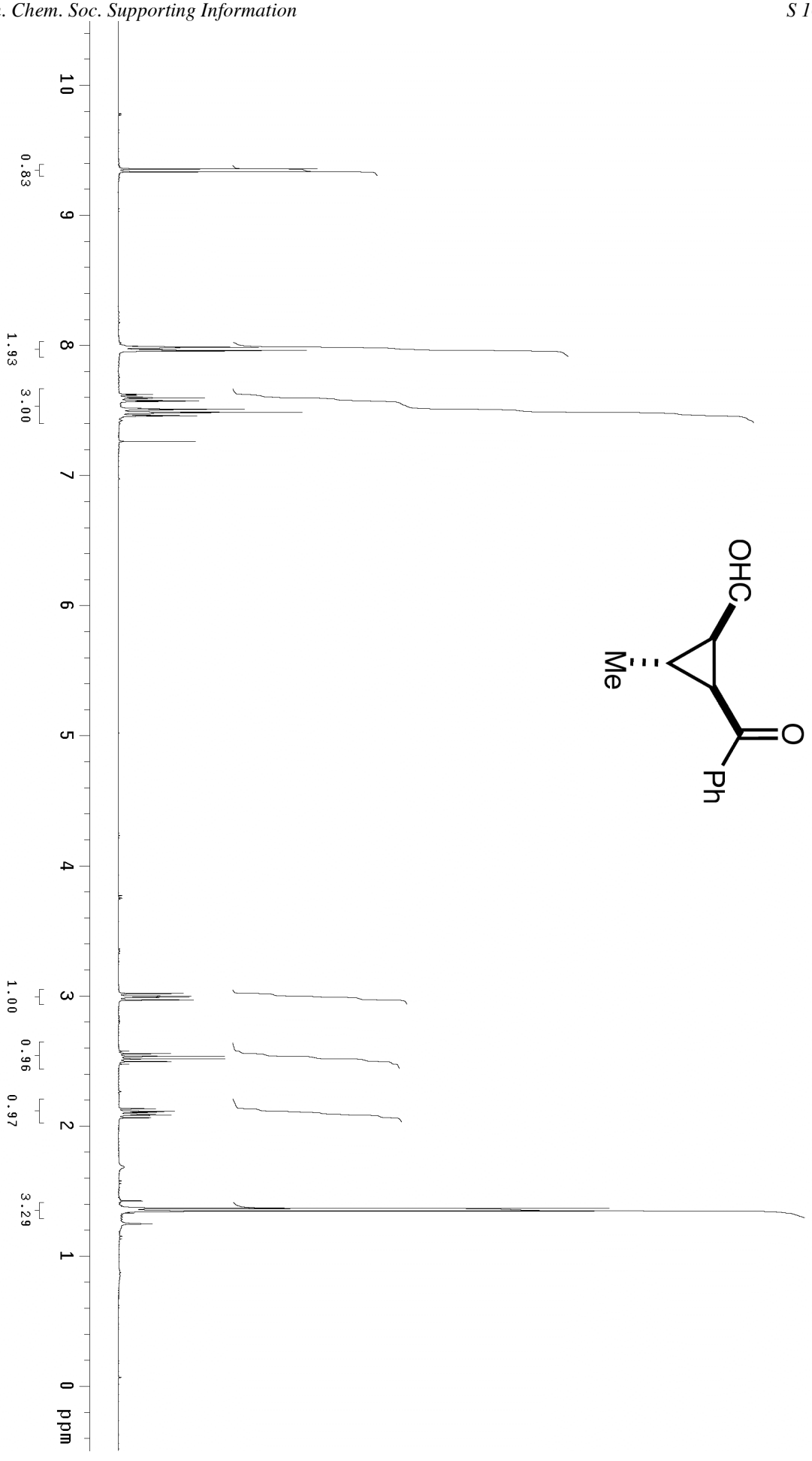
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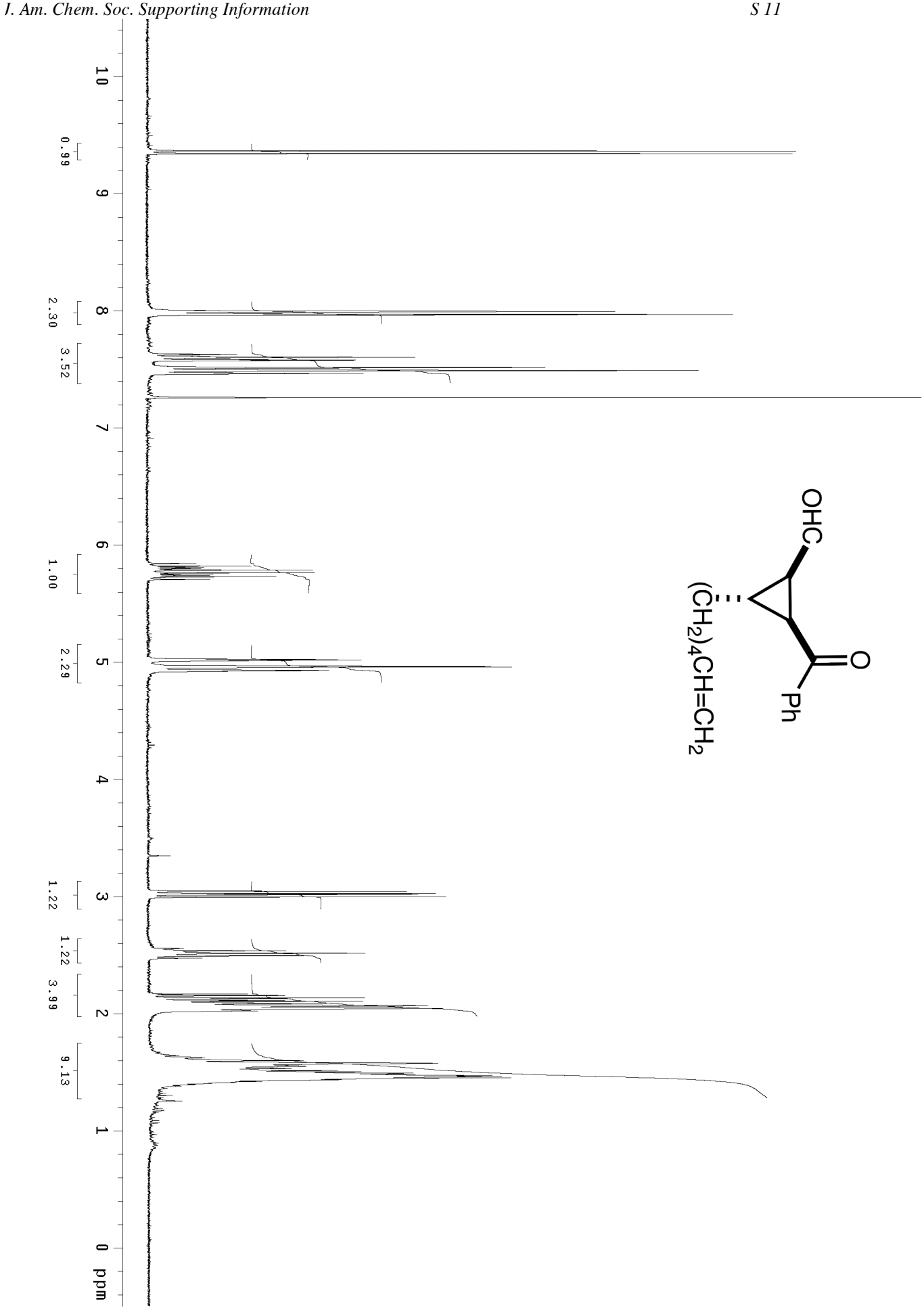
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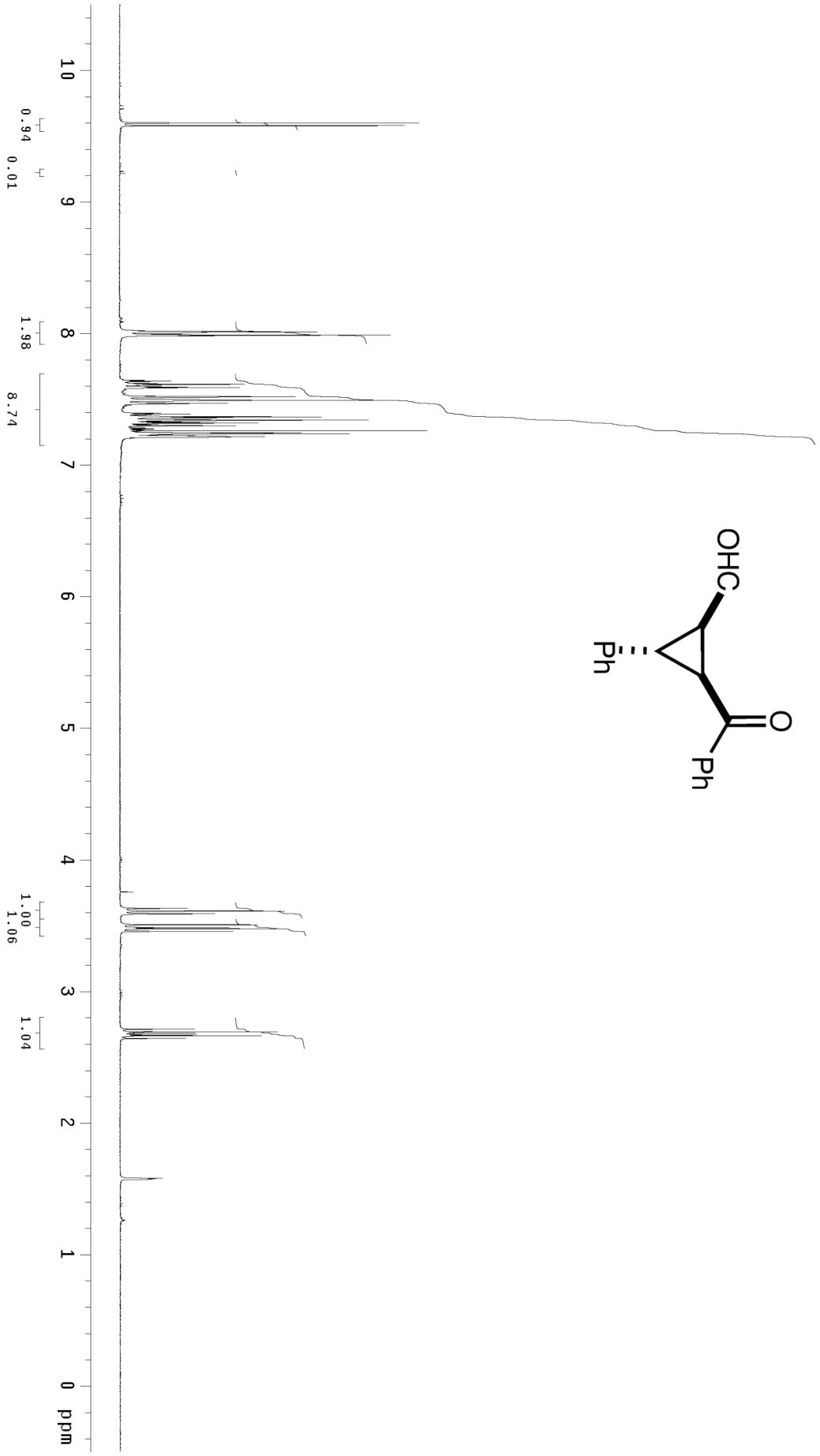
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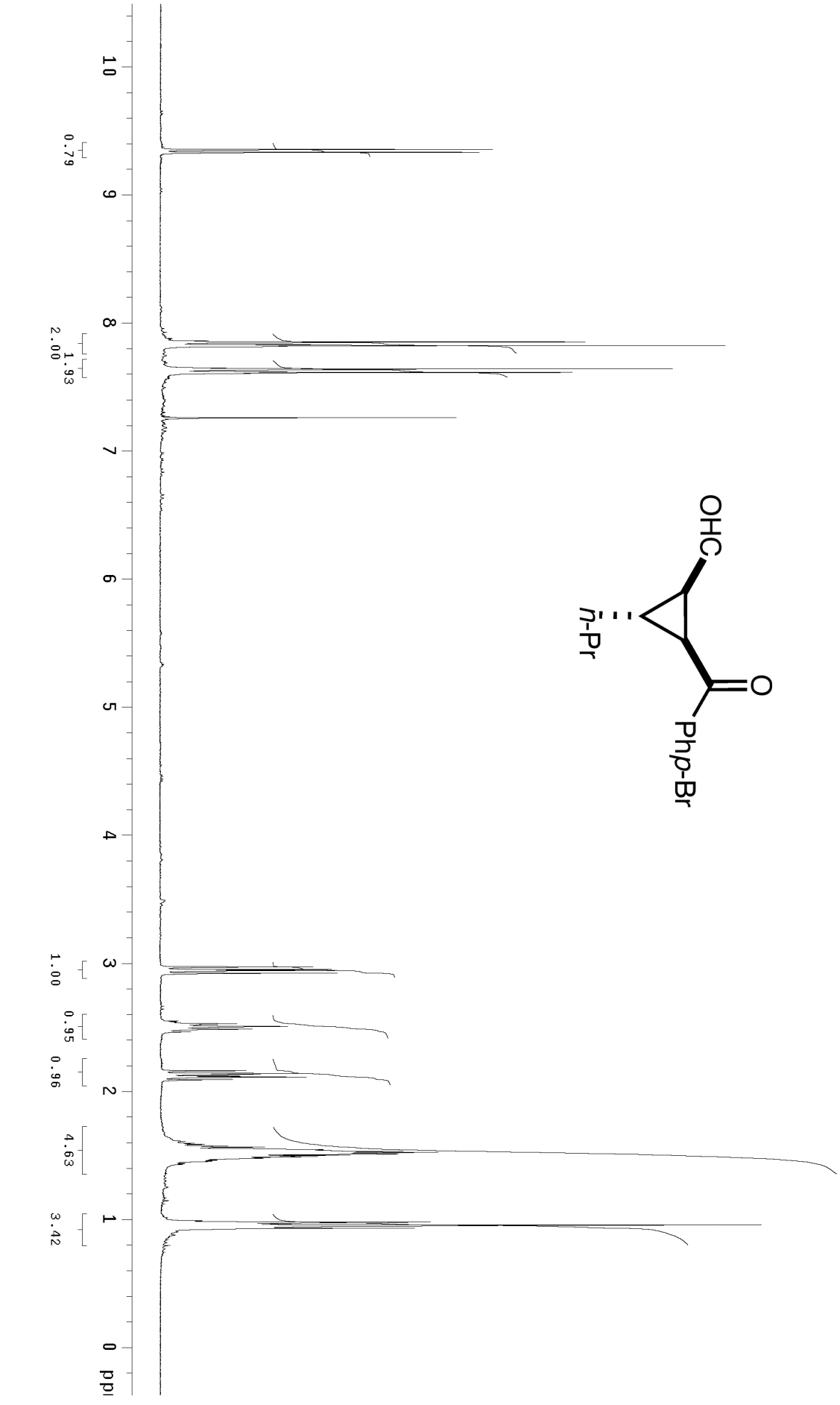
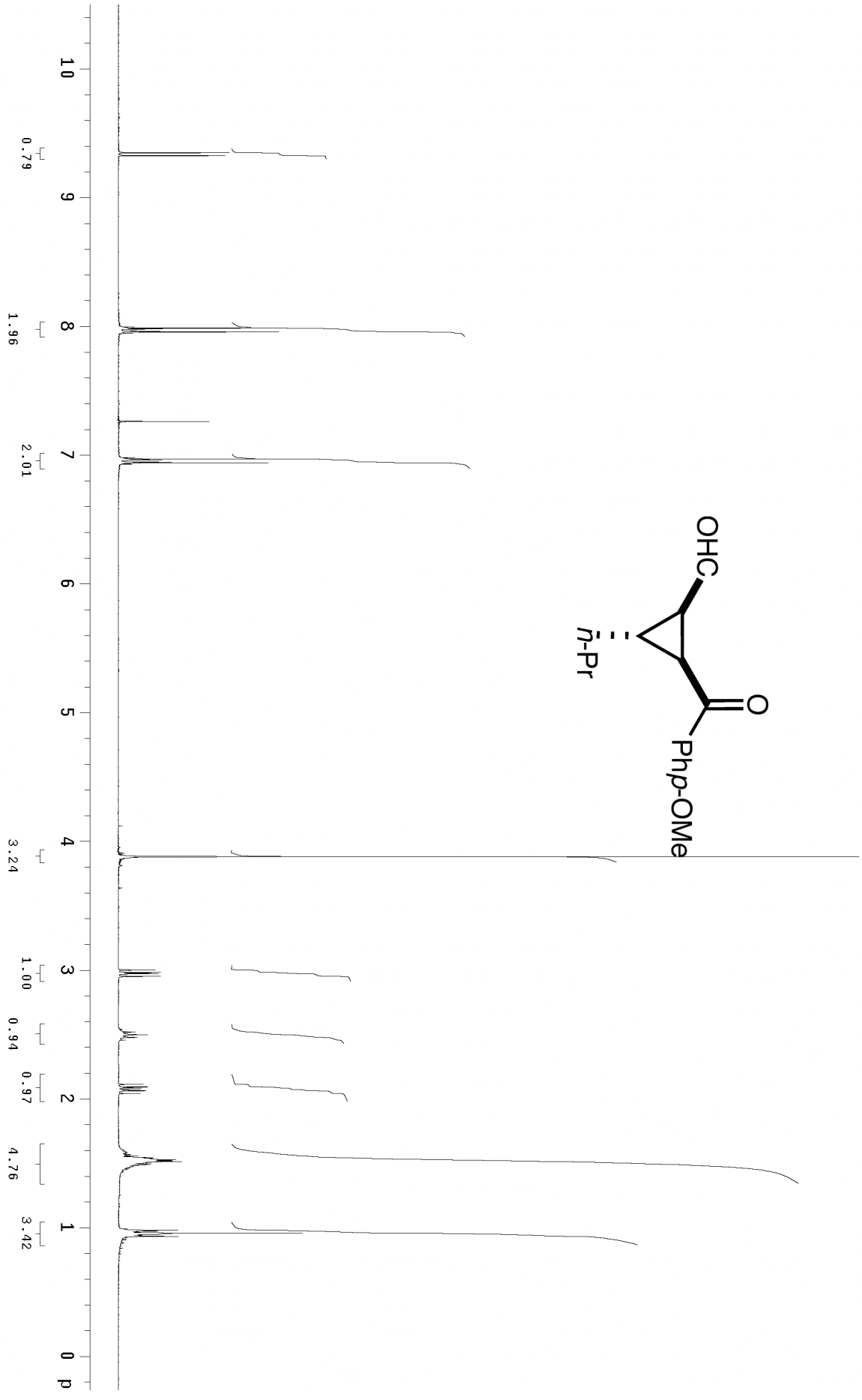
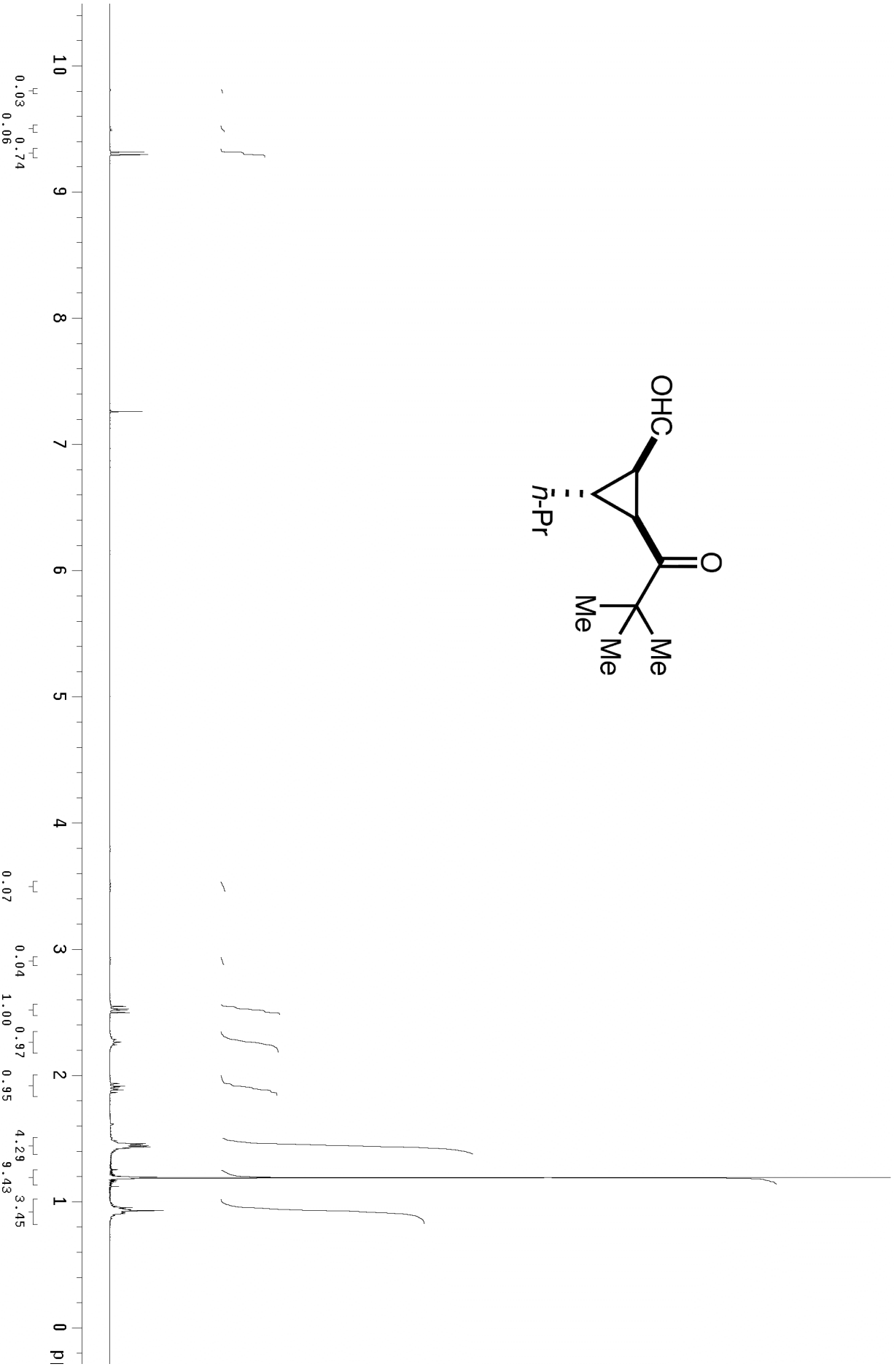
1.98
8.74
1.00
1.06
1.04
OHC
Ph
O
Ph


OHC
O
Ph
Me
Me
10
9
8
7
6
5
4
3
2
1
0
ppm
4.41
10.24
15.86
5.49
5.15
5.08
5.34
11.74
36.68

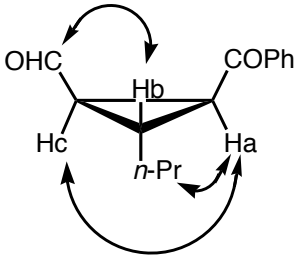

OHC
O
Ph
p-Br
n-Pr
10
9
8
7
6
5
4
3
2
1
0
ppm
0.79
2.00
1.93
1.00
0.95
0.96
4.63
3.42


OHC
O
Ph*p*-OMe
n-Pr
10
9
8
7
6
5
4
3
2
1
0
p
0.79
1.96
2.01
3.24
1.00
0.94
0.97
4.76
3.42


OHC
O
n-Pr
Me
Me
Me
10
9
8
7
6
5
4
3
2
1
0
ppm
0.03
0.06
0.74
0.07
0.04
1.00
0.97
0.95
4.29
9.43
3.45

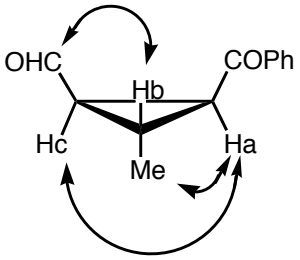
Relative and Absolute Stereochemical Assignments:

Table 1, entry 1



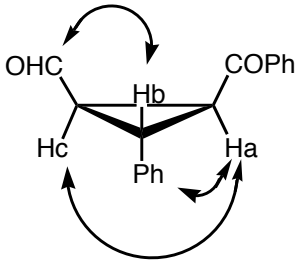
J_{Ha} = 5.9, 8.3 Hz
J_{Hc} = 5.8, 8.3 Hz

Table 1, entry 3



J_{Ha} = 6.0, 8.5 Hz
J_{Hb} = 6.1, 12.1 Hz
J_{Hc} = 6.4, 8.8 Hz

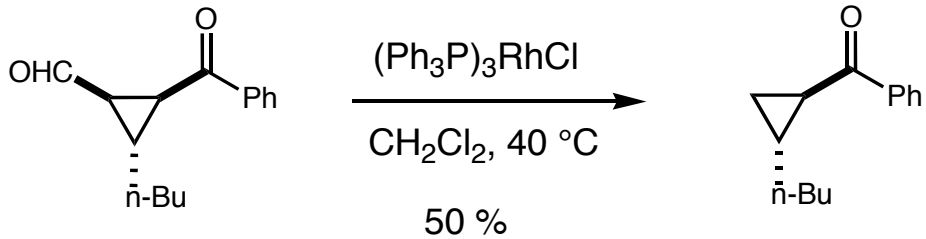
Table 1, entry 5



J_{Ha} = 6.3, 9.1 Hz
J_{Hb} = 6.0 Hz
J_{Hc} = 6.3, 9.1 Hz

arrow = positive NOE

(1*R*, 2*R*)-2-(Butyl-cyclopropyl)-phenyl methanone: Prepared according to the general cyclopropanation procedure from heptenal in 91% ee, subsequent deformylation using Wilkinson's catalyst gave the disubstituted cyclopropane which was identical in all respects to the literature compound[9] $[\alpha]_D$ = –61.6 (c = 0.90, $CHCl_3$). The enantiomeric ratio of the aldehyde was determined by GLC using a Bodman Chiraldex Γ-BP (30 m x 0.25 mm) column (150 °C isotherm for 70 min, 1 mL/min); *Major* enantiomer t_r = 63.6 min and *minor* enantiomer t_r = 65.4 min.



rotation = –61.6
(c = 0.9)

lit. rotation = –40.5
(c = 0.88), 92% ee

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